PATENT SPECIFICATION

(11) 1 562 275

(21) Application No. 13448/78 (22) Filed 6 April 1978
(31) Convention Application No. 785614
(32) Filed 7 April 1977 in
(33) United States of America (US)
(44) Complete Specification published 12 March 1980
(51) INT CL³ C08B 31/00 37/00
(52) Index at acceptance
C3U 2AX 2CX 4L

1 562 275

(19)

(72) Inventors DONALD DUANE CHRISTIANSON and HAROLD WAYNE GARDNER

(54) A PROCESS FOR THE PREPARATION OF STARCH-XANTHAN COMPOSITIONS

(71) We, UNITED STATES DEPARTMENT OF COMMERCE, a Department of the United States Government of 5285 Port Royal Road, Springfield, Virginia, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates primarily to starch-xanthan compositions which exhibit improved viscosities, solubilities, gelation properties and minimal syneresis.

Gums, in the form of natural, biosynthetic, or modified polysaccharides are known. Gums are mainly used as additives to control the properties of a commodity. Gums have unique properties of viscosity, pseudoplasticity, differing shear rates, stability to acid and heat, and serve as suspending and emulsifying agents which have been defined in specific use applications. The prior art has also established that specific properties can be enhanced with gum combinations. For example, a room-temperature setting gel is prepared by the interaction of xanthan gum and tara gum. This gel is resistant to either acid degradation or syneresis (weeping during freeze-thaw or heat-cool cycles). Low concentrations of xanthan gum, alone or in conjunction with other gums, have been used to improve the body, thickness, and dispersion qualities of food products. Canadian Patent Specification No. 797,202 discloses that excellent instant puddings are made from the gelling reaction between xanthan gum and locust bean gum.

When stirring with cold milk, a combination of the xanthan, locust bean gum, and tetrasodium pyrophosphate set to a good pudding body. The prior art use of gums in pudding and gels which contain starch relies on the interaction of the gum combination with tetrasodium pyrophosphate to form the product. The concentration of gums in relation to the amount of granular starch available for gelatinization and interaction with xanthan in these food formulations is of the order of 0.001 to 0.01 g xanthan per 100 g starch.

Furthermore, it is well known that starch in the granular state is insoluble in water at room temperature. It is also known that when a water suspension of unmodified granules is heated, the granules first slowly and reversibly take up water with limited swelling and at a definite temperature, typically about 70°C, the granules undergo irreversibly a sudden rapid swelling. As the temperature is increased beyond 70°C, more molecular starch diffuses from the granules and the starch appears to become soluble and translucent at about 80°C to 100°C. These temperatures vary with the different varieties of starch. It is also known that starch must be diffused from the granules by heating to be accessible to enzymic hydrolysis with amylases.

We have now discovered that it is possible to form useful reaction products of starch or amylose with at least 0.45 parts xanthan per 100 parts starch or amylose.

Particularly preferred products are those made by forming a dispersion of starch and xanthan in an aqueous medium, cooking the dispersion at a temperature which is 3 to 30 degrees below the normal gelatinization temperature of the starch and then either cooling the cooked dispersion to a gelation temperature, in which event a gel composition is formed, or drying the dispersion before cooling, in which event a stable powder is formed which will gel when dissolved in water.

The xanthan gum for use in this invention is preferably the extra-cellular polysaccharide derived from *Xanthomonas campestris* which can be prepared by the method in United States Patent Specification No. 3,507,664. Suitable starches include cereal and tuber starches from wheat, corn, potato, rice and tapioca. Other wet or dry milled fractions containing not less than 10 parts granular starch which is available for complete hydration and gelatinization are also suitable starting materials. Each starch variety with varying amylose and amylopectin content has distinctively different physical properties.

To make a gel or a powder the starch is normally first dispersed as granules in water or other aqueous medium in an amount of 2 to 30% by weight. Xanthan is incorporated in the dispersion at a level in the range of 0.2 to 2% by weight of the dispersion, and in an amount of 0.45 to 20, preferably 2 to 10, more preferably 6 to 10, parts per 100 parts starch, on a dry weight basis. Instead of dispersing starch granules in an aqueous medium the dispersion can be made by, for instance, adding starch to the xanthan gum broth during the final stages of xanthan production or by adding xanthan gum to the final stage of starch wet milling.

Cooking of the starch is conducted by heating the starch-xanthan dispersion at a temperature which is 3 to 30 degrees C below the normal gelatinization temperature of the starch when xanthan is not present. The gelatinization temperature corresponds to the temperature of initial viscosity increase manifest during pasting, or the minimum temperature to which the starch must be heated in order to form a gel upon cooling. Wheat normally gelatinizes at 85°C, corn starch at 74°C, rice starch at 83°C, potato starch at 64°C, and tapioca starch at 62°C. The dispersion is cooked at a temperature normally 3 to 30 degrees C below the quoted gelatinization temperature at least until the viscosity begins to increase and it becomes a paste. The paste is then cooled to a gelation temperature (about room temperature) and allowed to set up as a gel. Alternatively, the paste can be dried prior to cooling to form a stable powder. Any conventional means of drying, such as freeze drying, spray drying, and drum drying, may be employed. Powdered starch-xanthan compositions so prepared are readily soluble in hot or cold water and will gel when allowed to set about room temperature. Gels prepared either directly from the paste or from the rehydrated powder are stable at pH values of from 3 to 10, are salt tolerant to brine solution and sea water, and can tolerate freeze and heat cycles with minimal syneresis.

Starch-xanthan compositions can be formed as described in the presence of acids, salts, plant protein, and sucrose without hindering either the interaction or the development of its viscoelastic and gelation properties. When starch and xanthan are reacted at acid pH, the initial gelatinization temperature is reduced even more significantly to produce translucent gels. Bleached and unbleached soft wheat flours at pH 4.6 to 5.7, respectively, show a 4—10 fold increase in hot paste viscosity and start thickening at a temperature 20 degrees C lower than flours without xanthan addition. Proteins in soft wheat flours do not interfere with viscosity increases and gel formation. Processed soy, peanut, and cottonseed proteins can also be added at 60—90% levels to starch-xanthan compositions without any detrimental effect on gelation. These high protein gels can serve as meat analogues without extenders for animal-derived products.

Sucrose gels can be made from starch-xanthan compositions that have stability at acid and neutral pH. These starch-xanthan compositions can replace specially cross-bonded starches normally used to counteract the hydrolytic effects of acid in acidic foods such as fruit pie fillings. Rapid paste breakdown normally occurring in heated starch suspensions containing acid and sucrose is minimized using starch-xanthan compositions. Fruit juices and fruit pulp could be added during gelation to produce a variety of naturally flavoured jellies and candies (5—40% sucrose).

The compositions of this invention can be used as replacements for gelatinized, cross-linked or modified starch in foods and industrial products.

In another embodiment, the addition of starch to xanthan has been found to result in a reduction of the energy required for hydrolysis. Normally starch must be gelatinized before it can be hydrolysed to fermentable sugars during malting. However, we have discovered that in the presence of xanthan, starch slurries are completely hydrolysed to fermentable sugars with malt enzymes at 60°C, without prior gelatinization. The preferred amount of xanthan for effecting this result is about 0.5—5% based on the dry weight of the starch.

A preferred method for accelerating the hydrolysis of starch comprises heating a mixture of a starch containing from 7 to 10% by weight of free available starch and from 0.05 to 0.5% xanthan by weight to about 60°C, holding the mixture at 60°C for about 15 minutes, cooling the slurried mixture to 20 to 22°C and enzymatically hydrolysing the starch with malt enzymes at about 40°C for about 15 minutes. In such processes the starch is normally derived from wheat, corn or rice.

Combinations of xanthan-amylose can be cast into transparent pliable and strong films. Glycerol may be added as a plasticiser to reduce brittleness. A unique property of the film is its affinity for water, in which respect it differs from ordinary amylose films. The water absorption of these films is better than powdered xanthan alone which is often a disadvantage to xanthan solubility. In water, the film expands and has many of the properties of xanthan itself.

A preferred process according to the invention for preparing transparent, flexible, edible films having a good tensile strength comprises mixing in aqueous medium substantially equal parts by weight of amylose and xanthan, adding glycerol to the mixture, heating the mixture until it boils, sheeting the mixture, for example by casting the hot mixture on to a suitable casting surface, and drying the film, for example by air drying.

The invention is illustrated by the following Examples in which all parts are by weight unless otherwise specified. Various experiments outside the scope of the invention are designated as Controls.

Examples 1 and 2

Preparation of Starch-Xanthan Compositions

Slurries consisting of 8.0 parts dry weight wheat starch and 0.25 dry weight xanthan per 100 parts water were prepared by (1) heating slurries to 75°C with stirring, and freeze-drying the resultant translucent thickened paste to a fine powder, and (2) heating slurries to 75°C with stirring and spray-drying the thickened paste (Spray-drying conditions —110°C, flow rate $2\frac{1}{4}$ liter/hr). In Example 1, the viscosity of the product before drying was 1360 cps, and was 1365 cps after reconstitution. In Example 2, the viscosity of the composition before drying was 1364 cps, and was 1966 cps after reconstitution. The respective values when spray drying was used without prior heating were 200 and 464 cps.

Examples 3 to 7 and Controls A to D

Slurries consisting of 39.0 parts wheat starch and 0 to 4.5 parts xanthan in 500 ml water (pH 6.5) were heated at a rate of 1.5 C degree per minute to 95°C, held at that temperature for 15 minutes, and then cooled at a rate of 1.5 C degree per minute to room temperature. The viscosity of the suspensions was measured automatically throughout the run. Paste viscosities were measured at 50°C and 95°C, and at 22°C after the paste was cooled to room temperature. In the viscosity measurements, the viscosity of xanthan alone is subtracted from the values shown. Viscosities above 1000 Brabender units were not determined.

Example or Control	Xanthan, grams	Viscosity (Brabender units) 60°C	95°C	22°C
A	0.0	0	280	650
B	0.05	0	285	640
C	0.09	0	270	660
3	0.18	0	330	990
4	0.45	10	340	>1000
5	0.90	25	415	>1000
6	1.80	35	550	>1000
7	3.15	40	665	>1000
8	4.50	65	780	>1000

Examples 9 to 12 and Controls D to F

Interaction of Corn, Potato, and Rice Starch with Xanthan

Compositions of xanthan and corn, potato, and rice starch were prepared (pH 6.5 to 7.0) and viscosities determined as described for Examples 3 to 8 to demonstrate that these starches also form compositions with increased viscosity and gel characteristics.

Example or Control	Starch variety	Reactants: Starch (gram)	Reactants: Xanthan (gram)	Temperature of initial viscosity increase (°C)	Brabender Viscosity: Cooked	Brabender Viscosity: Cooled paste
D	Corn	40	0.0	74	350	1130
9	Corn	40	0.18	62	420	1440
10	Corn	40	1.80	61	560	—
E	Potato	20	0.0	64	520	600
11	Potato	20	0.18	61	550	825
F	Rice	25	0.0	83	280	760
12	Rice	25	0.18	65	570	1240

Examples 13 and 14 and Control G

Effect of pH and Salt on Viscosity of Starch upon Heating

Wheat starch-xanthan compositions were prepared and viscosities determined as described for Examples 3 to 8 except that the pH of the water was adjusted to pH 4.6

Example or Control	Reactants: Starch (gram)	Reactants: Xanthan (gram)	pH	Temperature of initial viscosity increase (°C)	Brabender Viscosity: Cooked	Brabender Viscosity: Cooled paste
A	39	0.0	6.5	85	280	650
3	39	0.18	6.5	63	370	900
6	39	1.80	6.5	57	550	950
G	39	0.0	4.6	85	265	800
13	39	0.18	4.6	64	370	960
14	39	1.80	4.6	60	610	1700

Examples 15 to 20 and Controls H to N

Slurries consisting of 4 parts wheat starch and 0.125 parts xanthan by dry weight in 100 parts water were heated to 95°C, held for 15 minutes at this temperature, and then cooled to room temperature. Viscosity of the slurries were compared at pH 2.2, 6.3 and 10.2 before and after addition of 2 parts sodium chloride. By way of comparison, slurries of 4 parts wheat starch only in 100 parts water were also heated to 95°C, held for 15 minutes, and then cooled to room temperature.

Example/ Control	Slurry pH	NaCl (gram)	Brookfield viscosity (cps): Starch with Xanthan	Brookfield viscosity (cps): Starch only(Control)
15/H	6.3	—	1008	484
16/J	2.2	—	1200	456
17/K	10.2	—	1536	936
18/L	6.3	2	1200	—
19/M	2.2	2	1230	336
20/N	10.2	2	1124	352

Examples 21 and 22 and Controls O and P

Starch-xanthan compositions were prepared and viscosities determined as described for Examples 3 to 8 except that bleached and unbleached soft wheat flour replaced starch, and the pH values were different.

Example or Control	Type flour	Reactants: Flour (gram)	Reactants: Xanthan (gram)	pH	Temperature where slurry starts to thicken (°C)	Hot paste viscosity at 95°C
O	Bleached	39	0.0	4.6	74	100
21	Bleached	39	1.80	4.6	51	480
P	Unbleached	39	0.0	6.5	76	70
22	Unbleached	39	1.80	6.5	53	370

Examples 23 to 25 and Controls Q to S

Influence of Xanthan on the Amounts of Starch Diffused into Solution During Heating

Slurries consisting of 19 parts wheat starch and 0 or 0.18 parts xanthan by dry weight in 500 parts water were heated to various temperatures as described for Examples 3 to 8. The suspensions were cooled to room temperature and centrifuged to separate residual starch granules from soluble material. The solubles were dried and weighed. The starch only products are characterised as SO, while the starch-xanthan products are given as SX.

Example or Control	Product	Suspension temperature (°C)	Percent starch solubilized
Q	SO	22	0
23	SX	22	5—7
R	SO	55	1—2
24	SX	55	10—15
S	SO	80	3—10
25	SX	80	50—75

4 g soluble starch material (SO) or (SX), as obtained in Examples 23 to 25 and Controls Q to S, were redissolved and then stained with iodine (0.2 parts iodine per 100 parts water) to determine colour changes effected by the amylopectin branched chained starch in the solubles. Shift in colour intensities toward 550 nm demonstrates increased diffusion of amylopectin during heating of the starch with xanthan.

	SO solubles		SX solubles	
Temperature, °C	550 nm	650 nm	550 nm	650 nm
55	no diffusion		.400	.700
80	.428	.692	.488	.600

Examples 26 to 28

Enzymic Hydrolysis of Starch in the Presence of Xanthan

Wheat starch (7—10 percent by weight) and 0.05 to 0.5 percent by weight xanthan in water were heated to 60°C and held for 15 minutes. The slurry was cooled back to room temperature and enzymically hydrolyzed with malt enzymes at 40°C for 15 minutes. The amount of hydrolyzed starch was analytically measured as glucose.

This procedure was then repeated for corn starch and rice starch, respectively, instead of wheat starch.

		Percent starch hydrolyzed	
Example	Starch variety	With xanthan	Without xanthan
26	Wheat	95—100	35—40
27	Corn	90—95	35—40
28	Rice	85—90	30—35

Example 29

Xanthan-Amylose Film Plasticised with Glycerol

Potato amylose (2.5 g) and xanthan (2.5 g) were thoroughly dispersed in 400 ml water. 1 ml glycerol was added as plasticiser. The mixture was brought to the boil, evacuated carefully to remove bubbles, and cast hot into Plexiglass (registered Trade Mark) trays and air-dried. The result was a film having flexible moulding quality with good tensile strength.

Examples 30 to 34

Production of Sucrose-Starch-Xanthan Gels

Slurries consisting of 7.8 parts starch (wheat) and 1.8 parts xanthan in 100 ml water were heated and cooled under conditions described for Examples 3 to 8. Pastes were diluted with various sucrose solutions so the original paste was diluted in half. The viscosity of the solutions were measured on a Brookfield Viscometer.

Example	Added sugar (gram)	Viscosity (cps) starch-xanthan
30	0	784
31	3	904
32	9	940
33	12	1132
34	15	1288

WHAT WE CLAIM IS:—

1. A reaction product of starch or amylose with at least 0.45 parts by weight xanthan per 100 parts by weight starch or amylose.

2. A process for making a product according to claim 1 in the form of a stable starch gel composition which exhibits minimal syneresis, the process comprising forming a dispersion of starch and xanthan in an aqueous medium, the amount of xanthan being from 0.45 to 20 parts per 100 parts of starch on a dry weight basis, cooking the starch-xanthan dispersion at a temperature which is from 3 to 30 degrees C below the normal gelatinization temperature of the starch, and cooling the cooked dispersion to gelation temperature.

3. A process for making a product according to claim 1 in the form of a powder which upon mixing with water will form a stable starch gel composition which exhibits minimal syneresis, the process comprising forming a dispersion of starch and xanthan in an aqueous medium, the amount of xanthan being from 0.45 to 20 parts per 100 parts of starch on a dry weight basis, cooking the starch-xanthan dispersion at a temperature which is from 3 to 30 degrees C below the normal gelatinization temperature of the starch, and drying the dispersion before cooling.

4. A process according to claim 2 or claim 3 wherein the starch is wheat starch and the cooking temperature is from 55 to 82°C.

5. A process according to claim 2 or claim 3 wherein the starch is corn starch and the cooking temperature is from 44 to 71°C.

6. A process according to claim 2 or claim 3 wherein the starch is rice starch and the cooking temperature is from 53 to 80°C.

7. A process according to claim 2 or claim 3 wherein the starch is potato starch and the cooking temperature is from 34 to 61°C.

8. A process according to claim 2 or claim 3 wherein the starch is tapioca starch and the cooking temperature is from 32 to 59°C.

9. A process according to any of claims 2 to 8 wherein the starch-xanthan dispersion contains from 5 to 40% by weight of sucrose.

10. A process according to any of claims 2 to 9 in which the amount of xanthan is from 2 to 10 parts per 100 parts starch on a dry weight basis.

11. A process according to any of claims 2 to 10 in which the amount of xanthan is from 0.2 to 2% by weight of the dispersion.

12. A process for making a product according to claim 1 substantially as described in any of the Examples.

13. A starch product made by a process according to any of claims 2 to 12.

14. A process for producing a hydrolysed starch product comprising forming a reaction product according to claim 1 by heating a mixture of starch and xanthan, and enzymatically hydrolysing the resultant product.

15. A process for hydrolysing starch comprising heating a mixture of a starch containing from 7.0 to 10.0% by weight of free available starch and from 0.05 to 0.5% xanthan by weight to about 60°C, holding the mixture at 60°C for about 15 minutes, cooling the slurried mixture to 20 to 22°C, and enzymatically hydrolysing the starch with malt enzymes at about 40°C for about 15 minutes.

16. A process according to claim 14 or 15 in which the starch is derived from wheat, corn or rice.

17. A process according to claim 14 substantially as described in any of Examples 26 to 28.

18. A hydrolysed starch product made by a process according to any of claims 14 to 17.

19. A process for making a transparent, flexible, edible film comprising a product according to claim 1, the process comprising mixing in aqueous medium substantially equal parts by weight of amylose and xanthan, adding glycerol to the mixture, heating the mixture until it boils, casting the hot mixture onto a casting surface, and air-drying the resultant film.

20. A transparent flexible edible film comprising a sheet of a reaction product of substantially equal parts amylose and xanthan plasticised by glycerol.

For the Applicants:—
GILL, JENNINGS & EVERY,
Chartered Patent Agents,
53 to 64 Chancery Lane,
London WC2A 1HN.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1980
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.